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Introduction

Bulk and supported molybdenum trioxide (MoO₃)-based materials have a distinguished record as heterogeneous catalysts for a broad range of transformations such as the oxidation of alcohols,^{1–3} olefin metathesis,⁴ benzylation of arenes,⁵ condensation of 1,2-diamines with carbonyl compounds,⁶ hydrodeoxygenation of biomass-derived phenolic compounds,^{7,8} furfuryl alcohol dehydration and condensation reactions,⁹ hydrogen and oxygen evolution reactions,¹⁰ and photocatalytic degradation of organic pollutants.¹⁰ The three crystal phases of MoO₃ are the layered, thermodynamically stable orthorhombic phase (α -MoO₃), the metastable ReO₃-type monoclinic phase (β -MoO₃), and the hexagonal phase (h-MoO₃).¹¹ To improve the catalytic performance of α -MoO₃,

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Heterogeneous catalysis with an organic-

challenge. Molybdenum oxide-based polymeric hybrid materials have been shown to be oxidation catalysts under mild reaction conditions, although difficulties remain with catalyst recovery/reuse since most perform as homogeneous catalysts or possess low activity. The present study shows that the hybrid material [MoO₃(2,2'-biimidazole)]·H₂O (1) is a superior catalyst regarding these issues. The structure of 1 was confirmed (by single crystal and synchrotron X-ray powder diffraction) to comprise one-dimensional chains of corner-sharing {MoO₄N₂} octahedra. Strong Mo=O···H-N hydrogen bonds separate adjacent chains to afford parallel channels that are occupied by disordered water molecules. Hybrid 1 was additionally characterised by FT-IR spectroscopy, ¹H and ¹³C MAS NMR, scanning electron microscopy and thermogravimetric analysis. The catalytic studies highlighted the versatility of 1 for oxidation reactions with *tert*-butylhydroperoxide as oxidant. By complementing with characterisation studies, it was verified that the reaction occurs in the heterogeneous phase, the catalyst has good stability and is recoverable *via* simple procedures. The chemical reaction scope covered epoxidation and sulfoxidation, and the substrate scope included biomass-derived DL-limonene and fatty acid methyl esters to give renewable bio-products, as well as thiophene and thioanisole substrates.

> techniques have been developed to synthesize nanomaterials with well-tuned sizes and shapes.^{10,12} Nanostructured MoO₃ with different morphologies such as thin sheets,3,5,12 wires,12,13 rods,¹² ribbons^{12,14} and belts^{6,12,15,16} have been fabricated by hydrothermal/solvothermal, sol-gel, template-assisted, and vapor phase deposition methods, among others. The techniques of hydrothermal synthesis can be exploited to tailor not only the morphology of MoO₃ nanostructures but also the oxide microstructure by the inclusion of structure-directing organic components.¹⁷ When organic ligands are incorporated, such as organonitrogen compounds, hybrid materials are obtained in which the ligand coordinates to a molybdenum site of the oxide array.18 The monodentate ligand pyridine19 (and its related bridging analogues like pyrazine,²⁰ 4,4'-bipyridine (4,4'-bipy),²¹ and 3,8-phenanthroline (3,8-phen)²²) yield perovskite-like layered structures consisting of corner-sharing {MoO₅N} polyhedra, while chelating ligands such as 2,2'-bipy tend to restrict the oxide dimensionality to chains or ribbons since their coordination blocks at least two condensation sites on the same metal centre.²³ Hydrothermal syntheses with 2,2'-bipy yield inorganic-organic hybrid materials of the $[(MoO_3)_m(2,2'-bipy)_n]$ family with structures consisting of one-dimensional (1D) oxobridged chains of corner-sharing {MoO₄} tetrahedra and/or



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{MoO₄N₂} octahedra.²⁴⁻²⁶ Analogous structures have been reported for 1,10-phen (m = 3, n = 2),²⁷ 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpdc; m = n = 1),²⁸ and 2,2'-biimidazole (H₂biim; m = n = 1).²⁹

We have previously studied the 1D polymeric hybrids $(\text{cation})_{x}[(\text{MoO}_{3})_{m}(L)_{n}]$ (L = 2,2'-bipy, x = 0; L = Hbpdc⁻, x = 1) as catalysts for the epoxidation of olefins and the oxidation of amines and sulfides.^{26,28,30,31} With olefins as substrates and tert-butylhydroperoxide (TBHP) or hydrogen peroxide as oxidant, the epoxidation reactions were at least partially catalysed in the homogeneous phase, *i.e.*, the polymers acted as sources of soluble active species.^{26,28,30} No report has yet been published on the catalytic properties of the hybrid material $[MoO_3(H_2biim)]$ ·nH₂O (1). This compound possesses, however, characteristics that could make it an interesting catalyst. Firstly, as reported in a recent crystallographic study,²⁹ the solid-state structure of 1 contains a solvent accessible void volume of 18.0% of the unit cell volume. In contrast, the chains of $[MoO_3(2,2'-bipy)]$ are densely packed in the crystalline state and there is no accessible space in the network for solvents.²⁴ Secondly, the ligand H₂biim and its neutral metal complexes are typically very poorly soluble in organic solvents, due largely to the presence of strong intermolecular hydrogen-bonds involving the N-H groups.³² The propensity of H₂biim to simultaneously bind a metal center (as a chelate) and to act as a hydrogen bond donor makes the ligand an excellent candidate for the fabrication of robust inorganic-organic hybrid supramolecular materials that could succeed as solid catalysts.33-35

In the present paper we report a comprehensive structural study of the hybrid **1**, employing both single-crystal and powder X-ray diffraction (XRD) methods, and an investigation of its catalytic performance in the epoxidation of olefins and the oxidation of sulfides using TBHP as oxidant. It is demonstrated that for these transformations **1** is a chemically stable and easily recoverable heterogeneous catalyst.

Experimental

Materials and methods

Ammonium chloride (99.9%, VWR), 40% aqueous glyoxal, ethylene glycol (99.5%, Fluka), *cis*-cyclooctene (95%, Alfa Aesar), methyl oleate (99%), methyl linoleate (95%, Alfa Aesar), DL-limonene (95%, Merck), methylphenylsulfide (99%), diphenylsulfide (98%), thiophene (\geq 99%), benzothiophene (95%), 5.5 M TBHP in decane, anhydrous α,α,α -trifluorotoluene (>99%), diethyl ether (99.8%), pentane (\geq 95%, Carlo Erba), anhydrous absolute ethanol (Carlo-Erba), ethyl acetate (\geq 99.7%, Honeywell), isobutyl acetate (99%), undecane (>99%), methyl decanoate (99%), and mesitylene (98%) were acquired from Sigma-Aldrich unless otherwise indicated, and used as received.

The titanosilicate TS-1 (Si/Ti \cong 50), a well-known industrial epoxidation catalyst³⁶ (herein used as a benchmark catalyst), was synthesised according to the method described in ref. 37, using SiO₂ powder as Si source. The hybrid material [MoO₃(2,2'-bipy)] was prepared as described previously by the oxidative

decarbony lation of the tetracarbonyl complex $\it cis$ -[Mo(CO)_4(2,2'-bipy)] with TBHP under mild conditions. ^{30}

ICP-OES analysis for Mo was performed at the University of Aveiro. Microanalyses for C, H and N were carried out with a Truspec Micro CHNS 630-200-200 elemental analyser. Standard powder XRD data were collected at ambient temperature on a Philips Analytical Empyrean diffractometer equipped with a PIXcel 1D detector, with automatic data acquisition (X'Pert Data Collector software version 4.2) using monochromatised $Cu-K_{\alpha}$ radiation ($\lambda = 1.54178$ Å). Intensity data were collected by the step-counting method (step 0.02°), in continuous mode, in the 2θ range 5–65°. Scanning electron microscopy (SEM) images and elemental (Mo) mappings were obtained on a Hitachi SU-70 microscope equipped with a Bruker Quantax 400 detector at 15 kV. Samples were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K 950 carbon evaporator. TGA was performed using a Shimadzu TGA-50 system at a heating rate of 5 °C min⁻¹ under air. FT-IR spectra were collected using KBr pellets and a Mattson-7000 infrared spectrophotometer. Attenuated total reflectance (ATR) FT-IR spectra were measured on a Bruker Tensor 27 equipped with a Specac® Golden Gate Mk II ATR accessory having a diamond top plate and KRS-5 focusing lenses. Solid-state ¹³C cross-polarization (CP) magic-angle spinning (MAS) NMR spectra were recorded using a wide-bore Bruker Avance 400 spectrometer (9.4 T) at 100.62 MHz with 3.7 μ s ¹H 90° pulses, 2000 ms contact time, spinning rates of 10-12 kHz, and 5 s recycle delays. ¹H MAS NMR spectra were acquired on the same instrument with 3.7 µs ¹H 90° pulses, 2000 ms contact time, spinning rate of 12 kHz, and 5 s recycle delays. Chemical shifts are quoted in parts per million (ppm) from tetramethylsilane.

Synthesis of $[MoO_3(H_2biim)] \cdot nH_2O (n \approx 1) (1)$

The ligand H₂biim was prepared and purified by adapting the procedures described in ref. 38 and 39, respectively.40 To prepare compound 1, a mixture of MoO₃ (70.0 mg, 0.48 mmol), H₂biim (65.2 mg, 0.48 mmol) and H₂O (25 mL) was heated under autogenous pressure and dynamic conditions (20 rpm) for 3 d at 160 °C in a Teflon-lined stainless-steel digestion bomb. The resultant product comprised thin colourless plates of 1, some of which were selectively removed for subsequent X-ray crystallographic examination. The remaining material was collected by filtration, washed with water, rinsed with diethyl ether, and finally air-dried (91 mg, 63%). Found: C, 24.15; H, 2.00; N, 19.05%. Calc. for C₆H₆MoN₄O₃·H₂O: C, 24.34; H, 2.72; N, 18.92%. TGA showed a mass loss of 6.2% at 100 °C (calc. for n = 1: 6.1%) and a residual mass of 47.0% at 480 °C (calc. for MoO₃: 48.6%). ¹³C{¹H} CP MAS NMR: $\delta_{\rm C}$ 120.3 (C-5/C-5'), 128.6 (C-4/C-4'), 135.9 (C-2/C-2'). ¹H MAS NMR: $\delta_{\rm H}$ 6.97 (br s, CH), 12.79 (s, NH).

Single-crystal XRD studies

Single crystals of compound $[MoO_3(H_2biim)] \cdot nH_2O$ (n = 1) (1) were manually harvested and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13,

Sigma-Aldrich) to avoid degradation caused by the evaporation of the solvent.⁴¹ Crystals were mounted on Hampton MiTeGen MicroLoops, typically with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses.

XRD data were collected at 150(2) K on a Bruker D8 QUEST diffractometer equipped with a Mo-K α sealed tube (λ = 0.71073 Å), a multilayer TRIUMPH X-ray mirror, a PHOTON 100 CMOS detector, and an Oxford Instruments Cryostream 700+ Cooler. Diffraction images were processed using SAINT+,⁴² and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS 2016/2.⁴³

The structure was solved using the algorithm implemented in SHELXT-2014/5,⁴⁴ which allowed the immediate location of almost all of the heaviest atoms composing the molecular unit. The remaining missing and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using the latest SHELXL from the 2018/3 release.⁴⁵ All structural refinements were performed using the graphical interface ShelXle.⁴⁶

Hydrogen atoms bound to carbon and nitrogen were placed at their idealised positions using the *HFIX 43* instruction in SHELXL. These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacement parameters ($U_{\rm iso}$) fixed at 1.2 × $U_{\rm eq}$ of the parent non-hydrogen atoms.

A total of one water molecule per metal centre was found from difference Fourier maps. These water molecules were located over two distinct crystallographic positions, each with a fixed site occupancy of 25% (determined from a previous unrestrained refinement for these locations). The atoms could not be modelled using a typical anisotropic treatment, clearly indicating a disordered nature. The atoms were included in the final structural model by assuming independent isotropic thermal displacement parameters $(U_{\rm iso})$. Although the hydrogen atoms associated with these moieties could not be located from difference Fourier maps, they have been included in the empirical formula of the compound.

Selected single crystal data for 1: $C_6H_8MON_4O_4$, M = 296.10, orthorhombic, space group $Cmc2_1$, a = 18.363(5), b = 3.8300(9), c = 14.745(3) Å, V = 1037.0 Å³, Z = 4, 5653 reflections measured, 966 unique ($R_{int} = 0.0972$), $R_1 = 0.0574$ and $wR_2 = 0.1230$ ($I > 2\sigma(I)$), $R_1 = 0.1075$ and $wR_2 = 0.1405$ (all data), highest difference peak 0.999 e Å⁻³ at 1.07 Å from O2, deepest hole -0.746 e Å⁻³ at 0.78 Å from O1.

Synchrotron X-ray powder diffraction studies

High-resolution synchrotron X-ray powder diffraction data for $[MoO_3(H_2biim)]\cdot nH_2O$ (n = 1) (1) were collected at 100 K, using an Oxford Instruments cooling device, on the powder diffractometer (Debye–Scherrer geometry) assembled at the undulator beamline ID22 (ref. 47) (6 GeV, ~200 mA) of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The high signal-to-noise ratio of the data is due to

the high brilliance of the synchrotron beam in combination with a Si(111) crystal multi-analyser.

The monochromatic wavelength was fixed at 0.495958(7) Å and calibrated against the Si standard NIST 640c (certified cell parameter a = 5.4311946(92) Å). Hard X-rays were selected for data collection to significantly reduce radiation damage, an occurrence observed in previous investigations using related materials but under different experimental conditions.^{28,48–50} Nevertheless, even at low temperature, the high brilliance of the synchrotron source led to visible damage of the samples. To minimize such effects consecutive data collections were performed on fresh portions of the sample by translating the capillary by *ca.* 1.3 mm.

A finely powdered sample of **1** was placed inside a Hilgenberg borosilicate glass capillary (diameter *ca.* 0.9 mm) which was spun during data collection to improve powder averaging over the individual crystallites, ultimately removing textural effects such as preferred orientation. Data were collected in continuous mode in the 2θ range 2 to 35° , with accumulation times increasing with the scattering angle. The counts of the six detectors (covering roughly $5.5^{\circ} 2\theta$) were rebinned and normalised to give the equivalent step scans (0.002°) suitable for further structural analyses.

The collected high-resolution powder XRD pattern was indexed using the LSI-index algorithm implemented in TOPAS-Academic V5,^{51,52} and a whole-powder-pattern Pawley fit unequivocally confirmed the orthorhombic space group $Cmc2_1$ as being the most suitable. Pattern indexation uncovered the presence of a small amount of an unidentified crystalline impurity, with the corresponding reflection discounted during the final stages of the refinement (see Fig. 1).

The crystal structure was determined in TOPAS-Academic V5 (ref. 51) by using a simulated annealing approach. In the first step, one molybdenum atom and two oxygen atoms were allowed to converge to their optimal positions within the unit cell while using a battery of anti-bump restraints to ensure chemically reasonable coordination geometries for the crystallographically independent {MoO₆} octahedra. Despite the high signal-to-noise ratio of the collected pattern, the location of the atoms composing the crystallographically independent organic component was extremely difficult, even when using distance restraints like those employed for the inorganic backbone. The derivation of the most suitable location for the N,N-chelated organic linker was performed in a second step by using a Fenske-Hall Z-matrix for half of this chemical entity and treating the ligand as a rigid body inside the unit cell. This strategy greatly facilitates the mobility of this chemical entity inside the unit cell boundaries during the global optimisation processes. It does not, however, allow for the conformational flexibility associated with the mutual rotations of the two rings. This was considered in a later stage during Rietveld refinement.

Rietveld structural refinement⁵³ was performed with TOPAS-Academic V5 (ref. 51) using a Chebyshev polynomial throughout the entire angular range to model the background contribution. The peak shapes for the powder



Fig. 1 Final Rietveld plot (synchrotron XRD data) of [MoO₃(H₂biim)]·H₂O (1). Observed data points are indicated as a blue line, the best fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid red and grey lines, respectively. Blue vertical bars indicate the angular positions of the allowed Bragg reflections for 1.

pattern were described using the fundamental parameters approach,⁵⁴ with preferred orientation effects being modelled with a 4th order spherical harmonics approach.

Selected powder diffraction and refinement data for 1: orthorhombic, space group $Cmc2_1$, a = 18.2315(3), b = 3.82916(3), c = 14.7377(2) Å, V = 1028.86(3) Å³, zero shift $(2\theta^{\circ})$ 0.003(1), 546 independent reflections, no. global refined parameters = 75, $R_{\rm p} = 7.67$, $R_{\rm wp} = 10.9$, $R_{\rm exp} = 1.44$, goodness-of-fit = 7.52, $R_{\rm bragg} = 3.91$.

Catalytic tests

Oxidation reactions were carried out using 10 mL borosilicate reactors equipped with a Teflon valve for sampling and a Teflon-lined magnetic stirrer. Initially, catalyst 1 (18 µmol of Mo), α , α , α -trifluorotoluene (TFT) (1 mL) and substrate (1.8 mmol) were added to the reactor, which was then immersed in a temperature-controlled oil bath at 35 °C (for thioanisoles and thiophenes) or 70 °C (for olefins), under stirring (1000 rpm). After 10 min, pre-heated TBHP (2.75 mmol for the reaction with cis-cyclooctene (Cy8); 4.07 mmol for the reactions with all other substrates) was added to the reactor, and reaction timing started at this instant. A higher amount of oxidant was used for the substrates other than Cy8 since the stoichiometry of the corresponding reactions to diepoxides or sulfones is two moles of TBHP per mole of substrate (to aid comparison, the same oxidant:substrate ratio was used for the monoene methyl oleate (Ole)).

Reactions were monitored using a Varian 3900 GC equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μ m) and a FID detector, with H₂ as the carrier gas. The reactant/products were quantified by calibrations and identified by GC-MS (Trace GC 2000 Series Thermo Quest CE Instruments GC; Thermo Scientific DSQ II), with He as the carrier gas. The product identifications were based on commercial mass spectrometry databases (Wiley6, NIST2.0, NIST Chemistry WebBook, MAINLIB) and mass spectral matching to available literature data. Undecane (for Cy8 and DL-limonene (DL-lim) reactions), methyl undecane (for Ole and methyl linoleate (LinOle)) and mesitylene (for methylphenylsulfide (mps), diphenylsulfide (dps) and benzothiophene (bt)) were used as internal standards. The experimental range of error was less than 6%, based on replicates carried out for selected experimental conditions.

Iodometric titration was carried out to check the oxidant efficiency: the reactor containing the catalyst, cosolvent and oxidant (1/TBHP/TFT), but no substrate, was heated at 70 °C for 4 h (stirring rate of 1000 rpm). After cooling the reactor to ambient temperature, a sample was withdrawn, filtered and titrated.

The catalytic reaction systems consisted of biphasic solidliquid mixtures. A filtration test was performed to check the homo/heterogeneous nature of the catalytic reaction (1/Cy8/ TBHP): the solid was separated from the liquid phase of the reaction mixture, at 1 h/70 °C, using a 0.2 μ m PTFE membrane. The filtrate was transferred to a separate reactor

(preheated to 70 °C) and stirred for 5 h at 70 °C, after which time it was analysed by GC. Additionally, catalyst recycling tests were performed in which the hybrid catalyst was recovered and reused: after each catalytic batch run, the solid catalyst was collected by centrifugation (5000 rpm), washed first with diethyl ether and then with pentane, air-dried overnight at ambient temperature, and finally vacuum-dried (*ca.* 4 mbar) for 2 h at 60 °C, giving the used/recovered catalyst denoted **1***. Catalyst **1*** was reused twice; the initial mass ratios of catalyst: substrate : oxidant were the same for all batch runs.

Results and discussion

Synthesis and characterisation of $[MoO_3(H_2biim)] \cdot nH_2O$ ($n \approx 1$) (1)

Compound 1 was prepared by the hydrothermal reaction of MoO₃, H₂biim, and H₂O in the mole ratio 1:1:50 at 160 °C for 3 days. The resultant crystalline product was isolated in 67% yield. This procedure is similar to the one employed by Morales et al.²⁹ SEM micrographs revealed that 1 displays a morphology consisting of aggregates of irregularly shaped thin plates (Fig. 2a). The FT-IR (4000–300 cm^{-1}) spectra of H₂biim and 1 were measured in the solid state as KBr pellets and are shown in Fig. 3. Wavenumbers and assignments (made in accordance with the interpretations proposed by Gruia et al.⁵⁵ for Cd²⁺ and Zn²⁺ complexes with H₂biim) are provided in Table 1. A comparison of the spectra of H₂biim and 1 with respect to the ligand-centered bands shows various shifts, intensity changes and splitting. Several of the most significant alterations mimic those described by Gruia et al. and can be attributed to the coordination of H₂biim as a bidentate chelating ligand with both N-H groups remaining protonated. For example, in the 1200–1050 cm⁻¹ range, where δ (C-H), δ (N-H) and ring vibrations occur, the bands at 1104 (vs) and 1143 cm⁻¹ (w) for H₂biim are replaced by bands at 1113 (m), 1139 (m) and 1185 cm⁻¹ (w) for **1**. The hybrid material displays a band with medium intensity at 1005



Fig. 2 Representative SEM images (a and c) and corresponding EDS maps for Mo (b and d) of 1 (a and b) and the used/recovered catalyst 1^* from the Cy8 reaction (c and d).



Fig. 3 FT-IR spectra (KBr pellets) of (a) H₂biim and (b) compound 1.

cm⁻¹, while free H₂biim only displays a very weak absorption in this region at 999 cm⁻¹, which was previously assigned to a δ (C,N–H) mode. The strong bands at 779 cm⁻¹ (broad) and 894 cm⁻¹ for **1** are attributed to v(Mo–O–Mo) and v(Mo=O) modes, respectively.

The solid-state ${}^{13}C{}^{1}H{}$ CP MAS NMR spectrum of H₂biim displays five sharp resonances in the region 110–145 ppm (Fig. 4A). Two pairs of resonances at 118.2/120.3 and 126.4/ 128.7 are assigned to C5/C5' and C4/C4', respectively, *i.e.* the

Table 1 FT-IR bands and possible assignments 49,55 for ${\rm H}_2{\rm biim}$ and compound 1

Assignment	H ₂ biim	1	
v(C-H)	3142 w	3126 m	
	3112 w		
	3000 s, br	2998 m, br	
v(N-H)	2895 s, br	2898 m	
		2929 m	
R	1545 s	1536 m	
R	1435 m	1431 m	
R	1405 vs	1405 w	
R	1333 s	1331 w	
v(C2-C2')	1217 m	1218 vw	
R	1143 w	1185 w	
$\delta(C,N-H)$	1104 vs	1139 m	
$\delta(C, N-H)$		1113 m	
$\delta(C, N-H)$	999 vw	1005 m	
$\delta(C, N-H)$	939 s	941 w	
R	915 w	920 sh	
R	887 s, br		
v(Mo=O)		894 s	
$\gamma(N-H)$	830 w	847 w	
v(Mo-O-Mo) _{asym}		779 vs, br	
γ(C-H)	763 m, 747 s,	(Overlap with	
	736 m	above band)	
R	689 s	682 s	
Chelate ring deforma	437 w, 395 m		
δ (Mo-O-Mo), v(Mo-O	339 m, 285 m		
$\gamma(MoO_2)$. ⁴⁹	- •		



Fig. 4 Solid-state $^{13}C(^1H)$ CP MAS NMR (A) and 1H MAS NMR (B) spectra of (a and c) $H_2 biim$ and (b and d) compound 1. Asterisks indicate spinning sidebands.

chemically equivalent Cn and Cn'atoms are crystallographically inequivalent in the solid-state. On the other hand, the ring-connecting C2/C2' atoms only give rise to one (more intense) signal at 138.8 ppm. The ¹³C{¹H} CP MAS NMR spectrum of 1 differs from that for the free organic ligand in that only one resonance is observed for each C5/C5' and C4/C4' pair (at 120.3 and 128.6 ppm, respectively). The crystallographic equivalence of each of these pairs of carbon atoms was subsequently confirmed by the X-ray diffraction studies (see below). Coordination of H₂biim to Mo^{VI} centres in 1 resulted in a slight upfield shift of the C2/C2' resonance from 138.8 to 135.9 ppm. The ¹H MAS NMR spectra of H₂biim and 1 are similar (Fig. 4B), displaying two well-resolved resonances in the region 0-15 ppm: one line at 14.72 ppm for H₂biim and 12.79 ppm for 1, assigned to NH protons, and a broader, more intense signal at 5.31 ppm for H₂biim and 6.97 ppm for 1, assigned to CH protons.



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Information about the thermal stability and composition of compound 1 was obtained by performing elemental and thermogravimetric analyses (TGA). CHN analyses indicated the empirical formula [MoO₃(H₂biim)]·*n*H₂O ($n \approx 1$). TGA of 1 under air showed an initial mass loss of 6.2% up to 100 °C, corresponding to the removal of water, and a succession of overlapping events between 200 and 480 °C, corresponding to the protracted oxidative decomposition of the organic ligand and the formation of MoO₃ (Fig. 5). The residual MoO₃ mass of 47.0% at 480 °C is close to the theoretical value of 48.6% calculated on the basis of the above formula. As expected, the TGA curve shows that the residual MoO₃ starts to sublime above 700 °C.

X-ray diffraction studies

Single crystal XRD studies confirmed the formula [MoO₃(H₂biim)] \cdot H₂O for the hybrid material **1**. The very thin colourless plates of 1 isolated from the hydrothermal synthesis diffracted rather poorly, especially at high angles. To unequivocally solve and refine the crystal structure, long acquisition times were required per frame (typically 240 seconds), with frame slicing of 1° up to a resolution of just 0.83 Å. Nevertheless, the $R_{\rm int}$ was rather large (0.0972) with many of the atoms being refined with large ellipsoids, typically indicating the presence of some structural disorder associated with each individual moiety. Bulk studies of the crystal structure of 1 were performed by using highresolution powder synchrotron XRD data collected at the ESRF, Grenoble. The structure was once again solved and refined, confirming the structural features previously unveiled from the single crystal studies. These investigations also showed the presence of trace amounts of unidentified crystalline impurities (Fig. 1).

The crystal structure of **1** agrees to some extent with the single crystal analysis reported by Morales *et al.* for their material formulated as $[MoO_3(H_2biim)]$ and prepared hydrothermally from MoO_3 and H_2biim .²⁹ The structure

comprises a 1D neutral and linear ${}_{\infty}{}^{1}$ [MoO₃(H₂biim)] coordination polymer that runs parallel to the crystallographic [010] direction of the unit cell with an intermetallic Mo···Mo distance along the Mo $\rightarrow \mu_{2}$ -O \rightarrow Mo direction of 3.8300(9) Å (Fig. 6). Although a similar intermetallic distance of 3.838 Å was found by Morales *et al.*, they determined an almost linear kink angle of 175.24° for this bridge (arising from alternating long (2.179 Å) and very short (1.662 Å) Mo–O_b bond lengths), while our structural analysis revealed a kink angle of 161.3(12)° (arising from alternating long (2.158 Å) and short (1.722 Å) Mo–O_b bond lengths).

The 1D polymer in **1** is analogous to that found in the inorganic–organic hybrid materials $[MO_3(L)]$ with L = 2,2'bipy (M = Mo,²⁴ W (ref. 56)) or H₂bpdc (M = Mo),²⁸ and $\{[MO_3(2,2'-bipy)][MO_3(H_2O)]\}_n$.⁵⁰ The basic building unit is composed of a six-coordinated Mo^{VI} metal centre bonded to three oxo groups (two terminal and one μ_2 -bridging) and one *N*,*N*'-chelated H₂biim organic moiety. The coordination geometry of the $\{MON_2O_4\}$ polyhedron resembles a highly distorted octahedron (Fig. 6(c)), mostly because of the *trans* effect of the terminal oxo groups: while the Mo–(N,O) bond lengths range from 1.722(13) to 2.346(19) Å, the *cis* and *trans* (N,O)–Mo–(N,O) octahedral internal angles lie in the ranges 69.1(9)–104.0(10)° and 156.6(6)–161.3(12)°, respectively.

Compound 1 contains one water molecule of crystallisation per Mo^{VI} centre. As depicted in Fig. 7, this molecule appears disordered over small channels running parallel to the [010] direction of the unit cell. Because individual $_{\infty}^{-1}$ [MoO₃(H₂biim)] coordination polymers are engaged in strong and rather directional hydrogen bonds connecting the oxo groups of one polymer to the N–H moieties of the adjacent one [$d_{D\cdots A}$ = 2.78(2) Å with <(DHA) = 162°], supramolecular contacts with the solvent molecules are much weaker, thus explaining the



Fig. 7 Crystal packing of $[MoO_3(H_2biim)]\cdot H_2O$ (1) viewed in perspective along the [010] direction of the unit cell.

disordered nature of the water molecules and the large isotropic displacement parameters.

Catalytic studies

Epoxidation of *cis*-cyclooctene (Cy8). For experimental benchmarking of epoxidation catalysts, the reaction rate of Cy8 with *tert*-butylhydroperoxide (TBHP) is often used. TBHP is a convenient source of active oxygen and displays great versatility in organic reactions, with the largest commercial application being the epoxidation of propylene.⁵⁷ The main drawback of TBHP is the risk of explosive decomposition



Fig. 6 Schematic representation of the (a) 1D neutral $_{\infty}^{1}$ [MoO₃(H₂biim)] coordination polymer present in the crystal structure of compound 1 running parallel to the [010] direction of the unit cell, emphasising the (b) linear nature of the polymer and the intermetallic distances. (c) Distorted octahedral coordination environment of the crystallographically unique Mo^{VI} metal centre. Selected bond lengths (Å) and angles (°): Mo1–O1 2.158(12), Mo1–O1ⁱ 1.722(13), Mo1–O2 1.750(11), Mo1–O2ⁱⁱ 1.750(11), Mo1–N1 2.346(19), Mo1–N1ⁱⁱ 2.346(19), O2–Mo1–O2ⁱⁱⁱ 104.0(10), N1ⁱⁱ–Mo1–N1 69.1(9), O1ⁱ–Mo1–O1 161.3(12), O1ⁱ–Mo1–O2 103.5(6), O2–Mo1–O1 87.8(5), O1ⁱ–Mo1–N1 89.5(7), O1–Mo1–N1 75.2(6), O2–Mo1–N1 91.4(7). Symmetry transformations used to generate equivalent atoms: (i) *x*, -1 + y, *z*; (ii) –*x*, *y*, *z*.

caused by heat, mechanical shock, friction, or chemical incompatibility. Competing against these safety concerns, however, is the recognition that TBHP presents fewer handling risks than 70% H_2O_2 in water or CH₃C(O)OOH, is not very corrosive, often leads to selective metal-catalysed oxidations, is freely soluble in organic media, and is obtainable from renewable resources.^{57,58} Furthermore, the co-product, *tert*-butanol, can be easily recovered by distillation and either recycled (to resynthesise TBHP) or used in other industrial processes, such as the synthesis of the fuel additive methyl *tert*-butyl ether (MTBE). The importance of TBHP as an oxidant for industrial reactions has motivated research into the development of safer processes, such as the continuous preparation of anhydrous TBHP solutions.⁵⁹

The Cy8 reaction with TBHP in the presence of 1 at 70 °C, with TFT as cosolvent, gave 1,2-epoxycyclooctane (Cy8O) as the sole product in 83%/99% yield at 6 h/24 h (Fig. 8), whereas without oxidant and/or without catalyst, the reaction was very sluggish. Iodometric titration of the reaction mixture indicated 100% oxidant efficiency for the hybrid catalyst 1, *i.e.*, negligible non-productive decomposition of TBHP into *tert*-BuOH and O₂.

Since the catalytic reaction system consisted of a biphasic solid–liquid mixture, a hot filtration test was performed to assess whether the epoxidation reaction took place homogeneously and/or heterogeneously. The results confirmed that 1 performed as a heterogeneous catalyst since, as shown in Fig. 8, the liquid phase obtained by filtration of the reaction mixture at 58% conversion (1 h reaction time) did not present any further Cy8 conversion up to 6 h, whereas for the normal catalytic run the conversion rose to 83% in the same time interval. No molybdenum was detected in the liquid phase by ICP-AES analysis (detection limit: *ca.* 0.50 μ g Mo per L) and hence metal leaching was deemed to be insignificant.



Fig. 8 Epoxidation of Cy8 with TBHP at 70 °C, in the presence of 1: normal catalytic test (**a**) and filtration test (**b**). Epoxide (Cy8O) selectivity was always 100%. The dashed lines are visual guides.

Catalyst recyclability and stability were studied by recovering the solid material after a catalytic run by simple centrifugation/washing/drying procedures (giving 1*). No drop in catalytic activity was observed when the recovered solid was reused; in fact, activity increased in consecutive batch runs, with conversions at 6 h of 87 and 99% in runs 2 and 3 (Cy8O selectivity was always 100%). The ATR FT-IR spectra of 1 and 1* were practically identical, demonstrating the good chemical stability of 1 (Fig. 9A). The crystalline structure (based on PXRD, Fig. 9B) and morphology (based on SEM, Fig. 2) of 1 changed upon contact with the reaction medium, which seems to correlate with the faster reaction kinetics of the reused catalyst. As mentioned above, the original catalyst possessed water molecules in crystallographically different positions, some of which were



Fig. 9 ATR FT-IR spectra (A) and PXRD patterns (B) of the ligand H_2 biim (a), compound 1 (b) and the used/recovered catalyst (1*) from the reactions of Cy8 (c), Ole (d) and dps (e).



fixed occupied sites. These crystallographic features may be flexible, changing in the multicomponent catalytic reaction medium, *e.g.*, *via* water desorption or partial exchange for other molecules. Importantly, the chemical structure and the uniform distribution of molybdenum were preserved (also verified with other substrates as discussed below).

The structure of 1 possesses dioxomolybdenum(vi) sites. Scheme 1 is a simplified representation of possible transition states (based on literature data) involved in olefin (represented epoxidation over as CH_2CH_2 dioxomolybdenum(vi) active sites. Based on mechanistic studies reported in the literature for oxomolybdenum(vi)catalysed olefin epoxidation with TBHP, the active species may be formed via the reaction of TBHP with the molybdenum sites, whereby a H-atom is transferred from the ROOH oxidant molecule (R = tert-butyl)to an oxomolybdenum group (Mo=O), leading to moieties of the type {Mo(O)(OH)(OOR)} (pathway (i) in Scheme 1). These intermediates may display an η²-asymmetric coordination mode $(Mo(O_{\alpha}O_{\beta})R)^{60-63}$ or exhibit a five-membered ring involving hydrogen bonding between a hydroxide group Mo-OH and the O_{β} atom of Mo- $O_{\alpha}O_{\beta}R$.⁶⁴⁻⁶⁷ Alternatively, pathway (ii) gives moieties of the type $\{Mo(O)_2(ROOH)\}$ that possess a very weak $Mo \cdots O_{\beta}$ interaction and a (stabilising) hydrogen bond between ROOH and an oxomolybdenum group (Mo=O).⁶⁸ The epoxidation then occurs via an O-atom transfer from the active oxidising site to the olefin.^{63–66}

Table 2 compares the catalytic performance of 1 with literature data for Mo-based catalysts possessing chelating N, N-bidentate ligands where Mo species are embedded (hybrid polymers) or supported. Furthermore, 1 was benchmarked with the well-known titanosilicate TS-1 heterogeneous catalyst and one of the best performing polymeric hybrids

Entry	Catalyst ^a	Solvent	Mol% Mo	TBHP/Cy8	$T/^{\circ}\mathrm{C}$	Conv. c1,c2,c3 ^{b} (%)	He/Ho ^c	Ref.
	Hybrid polymer-embedded Mo c	omplexes						
1	1	TFT	1	1.5	70	83,87,99	He	This work
2	[MoO ₃ (bipy)]	TFT	1	1.5	70	88	He + Ho	This work
3	[MoO ₃ (bipy)]	DCE^{d}	1	1.5	55	48	He + Ho	30
4		TFT	1	1.5	55	41	Но	26
5	$[Mo_2O_6(bipy)]$	TFT	1	1.5	55	72	Но	26
6	[Mo ₃ O ₉ (bipy) ₂]	TFT	1	1.5	55	54	Но	26
7	$\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$	DCE	1	1.5	55	18,25	He + Ho	50
8		Hexane	1	1.5	55	4.5,10,4.7	He	50
9		Hexane	1	1.5	75	45	He	50
10		TFT	1	1.5	55	33	Но	26
	Supported Mo complexes							
11	[O ₂ Mo···MoO ₂]@MCM-41-bipy	None	2	1.5	55	60,11	Но	69
12	[MoO(O ₂) ₂]@MCM-41-pzpy	$CHCl_3$	0.4	1.03	61	100,100	He	70, 71
13	MoO ₂ Cl ₂ @MCM-41-pzpy	None	2	1.5	55	85,79,79	He + Ho	72
14	[MoO(O ₂) ₂]@HSGM-pzpy	$CHCl_3$	0.8	1.03	61	95,95,95 ^e	He	73
15	[MoO(O ₂) ₂ (pzpy)]@SMNP	$CHCl_3$	1	1.2	61	96,96,95	He	74
16	[O ₂ Mo···MoO ₂]@LDH-bipy	DCE	2.8	1.5	55	54,39,30 ^f	He	75
17	MoO ₂ Cl ₂ @GaMOF-bipy	$CHCl_3$	0.7	2	50	$34,25,30^{f}$	He	76
18	MoO ₂ Cl ₂ @ZrMOF-bipy	TFT	0.7	1.5	75	63,44,17	He	77
19	MoO ₂ Cl ₂ @PMO-bipy	Toluene	0.1	1	75	$65,33,16^{g}$	He	78
	Other							
20	TS-1	TFT	_	1.5	70	5^h	He	This work

 Table 2
 Comparison of the catalytic behaviour in the epoxidation of *cis*-cyclooctene of compound 1 with the titanosilicate TS-1 and other Mo-based catalysts possessing chelating *N*,*N*-bidentate ligands, where Mo species are either embedded (hybrid polymers) or supported

^{*a*} For simplicity, the abbreviation 2,2'-bipy is shortened to bipy. MCM-41 = Mobil Composition of Matter no. 41; pzpy = functionalised pyrazolylpyridine ligand; HSGM = hybrid sol-gel material; SMNP = silica-coated magnetic nanoparticle; LDH = layered double hydroxide; GaMOF = gallium-based metal-organic framework; ZrMOF = zirconium-based MOF; PMO = periodic mesoporous organosilica. ^{*b*} Cy8 conversions after a reaction time of 6 h (unless otherwise indicated) for one (c1), two (c2) or three (c3) consecutive cycles. Selectivity to Cy8O was 100% or close to 100% in all cases. ^{*c*} Heterogeneous (He)/homogeneous (Ho) nature of the reaction. ^{*d*} DCE = 1,2-dichloroethane. ^{*e*} Reaction time of 4.5 h. ^{*f*} Reaction time of 7 h. ^{*g*} Cy8O yields at 8 h. ^{*h*} Reaction time of 24 h.

with a heterogeneous catalytic contribution, namely $[MoO_3(2,2'-bipy)]$, tested under identical reaction conditions to those used for 1. For simplicity, the former comparison is limited to systems devised on the concept of strong binding а chelating N,N-bidentate ligand between and oxomolybdenum(vi) units. Specifically, the systems are divided into two families: (i) hybrid materials such as 1 consisting of 1D chains of corner-sharing $\{MoO_2(\mu_2-O)_2\}$ tetrahedral units and/or {MoO₂(μ_2 -O)₂(2,2'-bipy)} octahedral units; (ii) supported materials in which individual molybdenum centres are heterogenised via binding with N,Nligands that are either an integral part of the support framework (bipyridine-based MOFs and PMOs, entries 17-19) or immobilised on the support via covalent tethering (silicabased supports, entries 11-15) or electrostatic interactions (LDHs, entry 16). Compound 1 is clearly superior to most of the previously studied chainlike hybrid materials, both in terms of catalytic activity and ability to catalyse the reaction heterogeneously.

The previously reported compound $[MoO_3(2,2'-bipy)]$, which was relatively active and was partly heterogeneous, led to much slower initial reaction kinetics than 1 (27% conversion at 1 h compared to 58% for 1); at 6 h/24 h similar conversions were reached for the two catalysts (83-88% at 6 h and 100% at 24 h; entries 1 and 2 of Table 2). However, [MoO₃(2,2'-bipy)] exhibited a small homogeneous catalytic contribution at 70 °C (as previously reported for this catalyst, albeit at 55 °C; entry 3, Table 2). Specifically, the liquid phase of the hot filtration test of [MoO₃(2,2'-bipy)] at 70 °C led to 10% Cy8 conversion between 30 min (the instant of catalyst filtration) and 24 h (compared to 73% for a normal catalytic test). Only the material { $[MoO_3(2,2'-bipy)][MoO_3(H_2O)]]_n$ could be used as a truly heterogeneous catalyst (with hexane as solvent, entries 8 and 9), but the catalytic activity was low (45% Cy8O yield after 6 h at 75 °C compared with 83% for 1 at 70 °C, entries 1 and 9). With regard to the supported materials, catalyst 1 displays competitive or similar performance in terms of activity and recyclability, even in relation to the best catalysts reported by Thiel and co-workers consisting of oxodiperoxo complexes tethered to silica-based supports via spacer groups functionalised with pyrazolylpyridine ligands (entries 12, 14, 15). Other supported materials, such as those comprising immobilised dinuclear complexes (entries 11 and 16) or MoO₂Cl₂ species (entries 13, 17-19) suffer from low activities, leaching phenomena and/or loss of activity upon recycling. The benchmark catalyst TS-1 (a type of industrial epoxidation catalyst³⁶) led to 5% Cy8 conversion at 24 h (entry 20, Table 2), possibly due to detrimental steric hindrance imposed by its microporosity.

The high boiling point and hydrophobic character of TFT makes it an attractive solvent for catalytic applications, reducing VOC emissions and protecting moisture sensitive catalysts/products. Nevertheless, TFT is classified as being toxic to aquatic life with long-lasting effects (GHS H411), and a highly flammable liquid and vapour (GHS H225). Hence, catalyst **1** was further studied using bio-based solvents,

namely bio-ethanol and the bio-esters ethyl acetate and isobutyl acetate (produced *via* fermentation processes⁷⁹), which have all been classified as recommended (or preferred) solvents based on safety, health and environment criteria.⁸⁰ Cy8 conversions at 6 h/24 h were 75%/93% for ethanol, 38%/ 100% for ethyl acetate and 29%/70% for isobutyl acetate. The catalytic results using ethanol resemble more closely those using TFT (83%/99% conversions at 6 h/24 h). For these four solvents, the dielectric constants at 20 °C decrease in the order ethanol (25.3) > TFT (9.2) > ethyl acetate (6.0) > isobutyl acetate (5.3), which does not correlate directly with the catalytic results. These results may be due to a complex interplay of factors including polarity and competitive effects between the oxygenated solvents and the oxidant in the coordination to the metal centres.

Scale-up consisting of a ten-fold increase in the volume of the reaction mixture for **1** (stirring rate of 1000 rpm) led to 63%/95% Cy8 conversion at 4 h/24 h, compared to 83%/99% at the microliter scale (TFT as solvent). Hence, similar conversion was reached in a 24 h batch, although the initial reaction kinetics was slower, which may be partly due to mass transfer limitations. Using more efficient types of mixers (a magnetic stirrer was used in this work) may advantageously enhance mass transfer.

The hybrid material **1** was further explored as a catalyst for broader chemical reaction (epoxidation, sulfoxidation) and substrate (biomass-derived olefins, thioanisoles and thiophenes) scopes.

Bio-based olefin epoxidation. Fatty acid methyl esters (FAME) are obtained by the transesterification of vegetable oils.81,82 FAME may be used directly (for biodiesel production) or after further modification such as epoxidation,⁸²⁻⁸⁴ which is useful in industry for the synthesis of chemicals and intermediates such as plasticisers and stabilisers of PVC, reactive diluents, detergents, and intermediates in the production of polyurethane polyols or components for lubricants, fuel additives, cosmetics and pharmaceuticals.⁸⁵⁻⁹¹ In industry, the traditional, most commonly used method for the synthesis of epoxidized FAME is the Prilezhaev reaction using in situ generated peracetic or performic acids.^{83,84} This process presents, however, several drawbacks, such as a low epoxide selectivity due to oxirane ring-opening reactions under acidic conditions, and the production of highly corrosive waste. It is, thus, of great academic and industrial interest to search for alternative epoxidation routes, especially those that employ easily recoverable and reusable heterogeneous catalysts.

The hybrid material 1 was an effective catalyst for the epoxidation of FAME, namely methyl oleate (Ole) and methyl linoleate (LinOle). The reaction of Ole led to 34%/72%/97% conversions at 1 h/6 h/24 h, 70 °C (TFT as solvent). The non-catalysed reaction was very sluggish (5% conversion at 24 h). Selectivity to methyl 9,10-epoxyoctadecanoate (OleO) was nearly 100% at 72% conversion, with only a slight drop to 97% occurring at very high conversion (97%) due to the concomitant formation of the polyol methyl 9,10-

dihydroxyoctadecanoate (OleDiol) (Table 3). This catalytic performance is on a par with that displayed by $[MoO_3(2,2'-bipy)]$, which led to 82% Ole conversion after 6 h at 75 °C (1 mol% Mo, TBHP/Ole = 1.5, DCE as cosolvent).⁹² Under the same conditions, except with TFT as the cosolvent instead of DCE, the hybrid material $[(CH_3)_2NH][MoO_3(Hbpdc)]\cdot nH_2O$ led to 93% Ole conversion after 6 h.²⁸ The Ole epoxidation reactions with the 2,2'-bipy and Hbpdc⁻ hybrids were, however, entirely homogeneous in nature, *i.e.*, the hybrids acted as sources of soluble active species. When tested under identical reaction conditions to those used for 1, catalyst $[MoO_3(2,2'-bipy)]$ led to 100% OleO selectivity at 62%/96% Ole conversion (6 h/24 h), suggesting that the latter

possessed lower activity in the initial stage of the reaction (up to 6 h) than 1 (72% conversion at 6 h).

The catalytic reaction of LinOle in the presence of **1** gave 31%/66%/88% conversion at 1 h/6 h/24 h (Table 3). LinOle was not reactive in the absence of a catalyst. The catalytic reaction gave mono- (LinOleO) and diepoxide (LinOleDO) products, specifically, methyl 9,10-epoxy-12*Z*-octadecenoate and methyl 12,13-epoxy-9*Z*-octadecenoate (86% total monoepoxide selectivity at 66% conversion), and methyl 9,10-12,13-diepoxyoctadecanoate (14% diepoxide selectivity at 66% conversion). The total monoepoxide selectivity decreased from 86% to 65% as conversion increased from 66% to 88% due to the concomitant formation of the diepoxide (34% selectivity at

Table 3 Catalytic performance of 1 in epoxidation and sulfoxidation reaction routes, from bio-based DL-lim and FAME, and thiophene and thioanisole substrates^{*a*}



^{*a*} Reaction conditions: initial concentration of substrate = 0.76-1.04 M, initial Mo:substrate:TBHP molar ratio = 1:100:153 for Cy8, and 1: 100:226 for the other substrates, TFT as cosolvent. ^{*b*} Conversion of substrate at 1 h/6 h/24 h. ^{*c*} Product selectivities at 1 h/6 h/24 h are indicated in parentheses.

88%, conversion, 24 h). These results suggest that 1 may favour the formation of polyepoxides, which are interesting intermediates to polyols. When tested under identical reaction conditions to those used for 1, catalyst $[MoO_3(2,2'-bipy)]$ led to 87%/72% LinOleO and 13%/28% LinOleDO selectivity at 63%/85% LinOle conversion (6 h/24 h), which is comparable to that for 1 (Table 3). TS-1 lacked catalytic activity for the epoxidation of Ole and LinOle, likely due to the inaccessibility of the bulky substrate molecules to the active sites.

Naturally occurring cyclic monoterpenes, such as R-(+)limonene (R-(+)-lim or D-lim) extracted from citrus peel waste, are another promising renewable olefin source. Their wide availability, relatively low cost and sustainable environmental profile make them attractive as raw material for further functionalisation, with epoxidation being one of the key transformations. The mono- and diepoxides of D-lim are key intermediates in the upgrading of limonene since a broad spectrum of oxygenated derivatives are accessible *via* epoxide ring-opening reactions.⁹³

Catalyst **1** was effective for the epoxidation of pL-lim (racemic mixture of the two enantiomeric forms p-lim and L-lim), leading to 73%/97%/100% conversion at 1 h/6 h/24 h, 70 °C (Table 3). Without catalyst, the Lim reaction was very sluggish (5% at 24 h). Similar results (95%/100% conversion at 6 h/24 h) were obtained for the homogeneously catalysed reaction using the material [(CH₃)₂NH][MoO₃(Hbpdc)]·*n*H₂O as source of active species (1 mol% Mo, TBHP/Ole = 1.55, TFT as cosolvent, 75 °C).²⁸

In the presence of 1, selectivity to the monoepoxide 1,2-epoxy-p-menth-8-ene (LimO) peaked at 87% after 1 h reaction, and then decreased to 55% at 100% conversion due to the concomitant formation of the diepoxide LimDO (35% selectivity at 100% conversion). These results tally with those for LinOle concerning the apparent ability of 1 to favour the formation of polyepoxides from bio-derived olefins. Minor products included 1-methyl-4-(1-methylethenyl)-1,2cyclohexanediol and others resulting from allylic oxidation (e.g., p-mentha-2,8-dienol and p-mentha-6,8-dien-2-one). The catalytic system presented high regioselectivity towards the epoxidation of the endocyclic C=C double bond, with the LimO/LimDO molar ratio being greater than ca. 1.6 until 100% conversion. When tested under identical reaction conditions to those used for 1, catalyst $[MoO_3(2,2'-bipy)]$ led to 100%/79% LimO selectivity at 75%/92% DL-lim conversion, at 6 h/24 h. At 24 h, LimDO and LimDiol were formed with 11% and 10% selectivity, respectively. Overall, [MoO₃(2,2'bipy)] seemed to be less active than 1 with bioderived olefins, and TS-1 was inactive (with Lim, Ole and LinOle).

Characterization of the catalyst recovered after reactions with bioderived olefins suggested that **1** is chemically and structurally stable (exemplified for the catalyst used in the reaction of Ole, in Fig. 9).

Sulfoxidation systems. The selective oxidation of sulfides is an important process since organic sulfoxides and sulfones serve as versatile intermediates/building blocks in the synthesis of agrochemicals, biologically active compounds, pharmaceuticals, and other valuable fine chemicals, as chiral auxiliaries, and as ligands in transition metal catalysis.^{94–98} Apart from synthetic chemistry, other applications of sulfoxidation have emerged, such as in extractive processes for the removal of refractory sulfur compounds from transportation fuels.⁹⁹ Much of the recent and current research on sulfoxidation processes focuses on the use of metal-based catalysts to achieve efficient chemoselective or enantioselective transformations. As in other fields of catalysis, the development of more environmentally acceptable protocols that employ recoverable catalysts, such as heterogeneous systems, is of pressing concern in sulfoxidation chemistry.^{100–102}

The hybrid material 1 was tested as a catalyst for the oxidation of thioanisoles and thiophenes with TBHP at 35 °C. The conversion of methylphenylsulfide (mps) was 98% at 1 h, giving the corresponding sulfoxide with practically 100% selectivity. As the reaction progressed, complete conversion was reached, and sulfoxide selectivity decreased from 99 to 67% with the concomitant formation of the sulfone with 33% selectivity. Hence, the operating conditions of the catalytic process may be controlled to adjust the reaction outcome according to the desire for sulfoxide vs. sulfone products (Table 3). Without catalyst, the mps reaction was much slower, giving 20% conversion at 1 h. With diphenyl sulfide (dps), 1 led to 100% sulfoxide selectivity at 81% conversion (no sulfone was formed); increasing the reaction time to 6 h led to yields of 80% for the sulfoxide and 20% for the sulfone. The substrate dps was less reactive without catalyst (100% sulfoxide selectivity at 69% conversion). The benchmark catalyst [MoO₃(2,2'bipy)] led to 100%/70% sulfoxide selectivity at 78%/100% dps conversion (1 h/6 h), a catalytic performance very similar to that for 1, although the bipy hybrid acted as a homogeneous catalyst. TS-1 was inactive, leading to similar results to those without catalyst (100% sulfoxide selectivity at 45% conversion, 6 h reaction).

The catalytic sulfoxidation screening tests showed that **1** was much more effective for the oxidation of thioanisoles than thiophenes. Thus, in the presence of **1**, thiophene did not react, while benzothiophene reacted to give the corresponding sulfoxide and sulfone products with 13 and 75% selectivity, respectively, at 35% conversion (24 h). Without catalyst, no reaction occurred (Table 3).

The chemical and structural features of **1** after catalytic reactions with sulfides were preserved (exemplified for the catalyst used in the reaction of dps, in Fig. 9).

Conclusions

The hydrothermally synthesised organic–inorganic hybrid material $[MoO_3(H_2biim)]$ ·H₂O (1) is an effective catalyst in epoxidation and sulfoxidation of various substrates with TBHP as oxidant. In the catalytic epoxidation systems (substrates: *cis*-cyclooctene, methyl oleate, methyl linoleate, DL-limonene), the epoxide products were formed in yields of at least 87% at 24

h/70 °C. In the catalytic sulfoxidation systems, the conversions of the thioanisoles (methylphenylsulfide, diphenyl sulfide) were in the range 81-98% at 1 h/35 °C, giving the corresponding sulfoxides with excellent selectivity ($\geq 99\%$); the reaction time may be optimised to tune the sulfoxide/sulfone product distribution at 100% conversion. Thiophenes (thiophene, benzothiophene) were more demanding than thioanisoles. Hybrid 1 exhibited heterogeneous catalytic behaviour: it passed the hot filtration test, could be easily separated from the reaction mixture, and was stable in consecutive batch runs. These features place 1 on a higher footing than most of the previously studied oxomolybdenum(vi)-based polymeric hybrid catalysts. The main significance of this development is that 1 can be used directly as a catalyst following its hydrothermal synthesis - there is no need of immobilisation (e.g. of a molecular catalyst) on a solid support or post-synthetic modification. Challenges remain in developing polymeric hybrids with enhanced catalytic activity for more demanding reactions such as those of thiophenes, under mild conditions.

Conflicts of interest

There are no conflicts to declare.

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